

(19) World Intellectual Property Organization
International Bureau



Rec'd PCT/PTO 30 MAR 2005



(43) International Publication Date
12 June 2003 (12.06.2003)

PCT

(10) International Publication Number
WO 03/048048 A1

(51) International Patent Classification⁷: C01G 23/047,
B01J 21/06, 37/00

(21) International Application Number: PCT/FI02/00985

(22) International Filing Date: 4 December 2002 (04.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20012397 5 December 2001 (05.12.2001) FI

(71) Applicant (*for all designated States except US*): KEMIRA
PIGMENTS OY [FI/FI]; Porkkalankatu 3, FIN-00180
Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): NAKATSUJI,
Tadao [JP/FI]; Itätuulenkatu 1 A 6, FIN-02100 Espoo (FI).
RÄSÄNEN, Lea [FI/FI]; Kulmakatu 2 H 89, FIN-00170
Helsinki (FI).

(74) Agent: BERGGREN OY AB; P. O. Box 16, Jaakonkatu 3
A, FIN-00101 Helsinki (FI).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TITANIUM DIOXIDE PHOTOCATALYST AND A METHOD OF PREPARATION AND USES OF THE SAME

(57) Abstract: The invention relates to a titanium dioxide photocatalyst and a method of preparation and uses of the same. The photocatalyst comprises particles having the crystal structure of rutile and/or anatase and a crystal size in the range of 5 - 50 nm. The photocatalyst is prepared by producing a titanium (III) containing solid precipitate from a solution in inert or substantially non-oxidizing conditions, by separating the precipitate and by calcinating it at an elevated temperature. The photocatalyst according to the invention has an improved activity, which is assumed to be due to an oxygen vacancy as compared to the stoichiometric amount of oxygen in titanium dioxide. The uses of the photocatalyst comprise decomposition of organic compounds and microorganisms, including uses as a component in various surface coatings such as paints and self-cleaning or anti-fogging coatings.



WO 03/048048 A1

Titanium dioxide photocatalyst and a method of preparation and uses of the same

Field of the invention

- 5 The invention relates to a method for the preparation of a titanium dioxide photocatalyst with an increased activity in the wavelength ranges of visible and ultraviolet light. Further objects of the invention are a photocatalyst obtainable according to said method, as well as uses of the catalyst for various reactions involving reduction or decomposition of substances.
- 10 The invention thus relates to a photocatalyst which can catalyze photocatalytic reaction using visible light and/or UV light for e.g. decomposition of environmental contaminants, splitting water into H_2 and O_2 , and oxidation of NO into NO_2 , and more particularly to the technical field of visible light-active photocatalysts which cause a conspicuous improvement in photocatalytic efficiency and quantum yields.
- 15 This is achieved by preparing nano-scale ultra-fine uniformly structured titanium dioxide particles with anatase and/or rutile crystal structures, and what is supposed to be an oxygen deficit as compared to the stoichiometric amount of oxygen in TiO_2 . The nano-scale titanium dioxide particles of the invention are capable of realizing visible light-photocatalytic reactions with high quantum yields.
- 20 In the prior art titanium dioxide has been prepared by thermal hydrolysis at 100-110°C using titanium oxysulphate ($TiOSO_4$), *so called* sulfuric acid method, followed by calcining at 100-500°C. In conventional neutralization or sol-gel method, the titanium dioxide can be produced. However, such titanium dioxide has no photocatalytic activity in visible light irradiation.
- 25 A photocatalytic reaction of titanium dioxide was reported in Nature in 1972. Since then, research has been conducted on the production of hydrogen by the decomposition of water by using titanium dioxide as a catalyst and irradiating with a UV light. Recently research fields have been expanding to the decomposition of environmental pollutants, *i.e.*, bad smell materials such as aldehydes, ammonia and
- 30 dimethyl sulphide and tobacco components/tar, and the disinfection of bacteria and toxins producing bacteria, and furthermore the anti-fogging and self-cleaning of surfaces with making use of super-hydrophilic properties of titania.

The principle of the action of fine titanium dioxide particles is attributed to the photocatalytic characteristics of titanium dioxide as a semiconductor. If titanium dioxide is irradiated with light which exceeds the band gap, in case of anatase crystal structure: 3.2 eV, *i.e.*, the wave length is necessarily shorter than 380 nm; *e.g.*, ultra-violet light, then the electrons in the valency band are excited and undergo a transition to the conduction band, so that positive charged holes are left in the valency band. These electrons and holes move from the inside of titanium dioxide particle to the surface where the electrons are supplied to oxygen adsorbed on titanium dioxide or oxygen in air so that super-oxide anions are produced. The holes not only cause direct oxidation of organic materials, but also oxidize water molecules adsorbed on the surface, followed by forming strongly oxidizing hydroxyl radicals and oxidizing substances. Thus, organic materials, such as hydrocarbons, oxygen-containing organic compounds or inorganic materials like NO are oxidized into water, carbon dioxide and nitrogen dioxide by electron-hole pairs excited by light.

Excitation which creates electron-hole pairs in titanium dioxide occurs only on the ultra-violet irradiation. Therefore, when using sunlight or fluorescence light to activate the titanium dioxide as a photocatalyst, only a small percentage of the energy in sunlight and almost nothing of the energy in fluorescence light is available. For practical use, it is essential to develop photocatalysts with higher visible light activity. Many studies have been conducted on the development of TiO₂ based photocatalyst that can work with visible light irradiation. TiO₂ doped with metals such as Cr, Mn, Co; Fe, etc. have been found to adsorb visible light (see *e.g.* J. Electrochem. Soc. 127 (1980) 2148). However, in most cases, activities of the TiO₂ photocatalysts tend to decrease, due to the simultaneous enhancement of the electron-hole recombination by the doped metal. It was reported that a TiO₂ photocatalyst prepared by Cr ion-implantation catalyzes NO decomposition into nitrogen, nitrous oxide and oxygen with visible light irradiation above 450 nm in the absence of oxygen, and the catalyst shows the same photocatalytic efficiency as the undoped-TiO₂ with ultra violet irradiation (Catal. Surv. Jpn. 1 (1997) 169). However, from the practical point of view, it will be impossible for this technology to be applied to practical use, because of very high production cost.

Recently, it has been found that the hydrogen plasma-treated TiO₂ shows visible light activity for NO oxidation into NO₂ in oxidizing conditions and the TiO₂ has oxygen vacancies, resulting in the formation of oxygen vacancy states in the band structure, then shortening the band gap and creating visible light activity (J. Mole.

Catal. A 161 (2000) 205). Furthermore, a sputtering method to prepare oxygen has been disclosed (JP2001-62310A). However, this preparation method is not practical from the point of cost performance and there is a serious problem that oxygen-vacant titanium dioxide is formed mainly at the surface of the original titanium dioxide and the hydrogen plasma-treated TiO_2 is not stable in oxidizing conditions, resulting in deterioration of the activity during photocatalytic reactions with visible light irradiation. It is well known that oxygen-vacant titanium dioxide can be prepared by reducing titanium dioxide with hydrogen at a high temperature such as 600-1000°C. However, this oxygen-vacant titanium dioxide is also unstable in oxidizing conditions and it loses oxygen vacancies quickly in such conditions. In addition, the size of the titanium dioxide crystals is too big to show a high activity.

In order to achieve efficient utilization of generated electrons/holes in a photocatalyst, it would be desirable that the distance from the generated electron/hole sites to the surface is as small as possible: quantum size effect, in other words, the particle size of the photocatalyst should be minimized as small as possible while maintaining the crystallinity of the photocatalyst as far as possible. In case of poor crystallinity, some kinds of impurity levels are formed, resulting in a low activity. On the other hand, for a stable visible light-active photocatalysis at ordinary temperature in oxidizing conditions, titanium dioxide-based photocatalyst should have the oxygen vacancies uniformly dispersed in the titanium dioxide. The titanium dioxide should be prepared by uniformly incorporating oxygen vacancies during the formation of the titanium dioxide crystals. In case that metals are doped in the titanium dioxide in order to shorten the band gap, the incorporated metals function as electron/hole recombination centers, resulting in a low activity in the irradiation of visible light. When oxygen vacancies are formed mainly on titanium dioxide-surface, the titanium dioxide can catalyze photocatalytic reaction with visible light, but the vacancies are not stable, resulting in high deterioration during the reaction. Thus, a photocatalyst composed of titanium dioxide, in which oxygen vacancies are uniformly distributed, would intrinsically show a high photocatalytic activity with visible light irradiation. This would allow the use of sunshine or fluorescence or UV light at a high efficiency. Ultimately, application fields of the photocatalyst would be expanded by leaps and bounds.

Summary of the invention

It is the first object of the invention to provide a method for the preparation of a visible light-highly active photocatalyst which does not deteriorate at ordinary temperatures in oxidizing conditions. The method of the invention comprises

producing a titanium (III) containing solid precipitate from a solution containing titanium (III) ions in inert or substantially non-oxidizing conditions, separating precipitated solids from the liquid phase, and calcinating the separated solids at an elevated temperature so as to obtain a photocatalyst product having a crystal size in
5 the range of 5 – 50 nm.

The titanium dioxide prepared according to the invention has been found to have a photocatalytic activity which is significantly higher than that of the titanium dioxides of the prior art. Without limiting the invention or binding it to a theory, it is strongly believed that the increased activity is due to oxygen vacancies, i.e. an
10 oxygen deficit in comparison with the stoichiometric amount of oxygen in titanium dioxide, said vacancies being substantially uniformly distributed in the nanocrystalline titanium dioxide produced. Presuming that this is the case, the advantage gained by the invention would be explained by the theoretical discussion in the "field of the invention" section above.

15 The titanium dioxide photocatalyst can advantageously be prepared by using Ti^{+3} ion solution such as $Ti_2(SO_4)_3$ solution as a precursor which is then neutralized at 0-115°C, preferably 50-100°C with alkaline materials such as ammonia gas, ammonium hydroxide, an alkali or earth alkali metal hydroxide or a mixture thereof, in inert and/or reducing conditions, followed by ageing of the precipitate at
20 50-150°C at a pressure in the range from atmospheric pressure to 50 bar, or at most 100 bar, for 0.1-10 hours in the inert and/or reducing conditions, washing to remove salts and drying in air or vacuum at 0-100°C. Inert or reducing conditions in these steps can be maintained by bubbling inert gas, such as nitrogen, through the solution, or by addition of a reducing agent. By changing parameters in the
25 neutralization and ageing steps, it is easily possible to control the properties of the titanium dioxide such as crystal structure, crystal size, as well as the amount and extent of the supposed oxygen-vacancy. Preferably, the titanium dioxide is calcined at 100-500°C in inert or substantially non-oxidizing conditions in order to control the crystallinity.

30 The invention further includes a titanium dioxide photocatalyst, which comprises particles having the crystal structure of rutile and/or anatase and a crystal size in the range of 5 – 50 nm, preferably 5 – 20 nm. Such a catalyst is obtainable by the method described above, and is believed to have oxygen vacancies substantially uniformly distributed through the particles.

The uses of the catalyst specifically, although not exclusively, covered by the invention are as a catalyst for decomposition of organic compounds or microorganisms, as a photocatalytically active component in compositions applied onto substrates such as honeycomb catalyst structures, as a component of a paint for car bodies, as a component of a self-cleaning surface coating, as a component of a coating for glass, lamps or shades, or as an anti-fogging agent.

Detailed description of the invention

The material of the present invention having a visible-light photocatalytic activity and the method of manufacturing such material will be explained below in further details.

As has been mentioned, the material of the invention having a visible-light photocatalytic activity is assumed to comprise titanium dioxide with a degree of oxygen-vacancy. Such titanium dioxide is characterized by ESR measurement and XPS (X-ray photoelectron spectroscopy). In the ESR, the spectra of the titanium dioxide of the invention has a broad and weak signal assigned to Ti^{3+} ions at $g = 1.960$ and a sharp signal at $g = 2.003$. This suggests that the titanium dioxide contains large amount of Ti^{4+} and a small amount of Ti^{3+} , resulting from an oxygen deficit. Furthermore, it has been confirmed in the XPS, as reported in the literature (Phys. Rev. 28 (1983) 3427), electron binding energy of $Ti2p_{3/2}$ of the titanium dioxide of the invention shifts to a little bit higher energy level than ultra violet active-titanium dioxide prepared by the conventional sulfuric acid method. The spectra seem to be attributable to defects of titanium dioxide. Furthermore, using argon etching it has been found that the defect is uniformly located in the titanium dioxide of the invention. The titanium dioxide of the invention was exposed to air in irradiation with visible light of a wavelength of 450 nm. There was no significant change of ESR signals between fresh and aged titanium dioxide of the invention. Therefore, titanium dioxide of the invention is stable in the atmospheric environment where photocatalysis occurs with a visible light such as sunshine and fluorescence light.

As described above, titanium dioxide of the invention shows highly active photocatalytic activity due to quantum size effect, because the crystal size of the titanium dioxide is in the range of 5-50 nm, preferably 5 – 20 nm, with maintaining the crystallinity of titanium dioxide as far as possible. Furthermore, the titanium dioxide includes anatase type titanium dioxide and rutile type titanium dioxide according to differences in crystal structure. In the band structure of rutile and

anatase type-titanium dioxide, the band energy gap of the rutile type is 3.05 eV, on the other hand, the band gap of the anatase type is 3.20 eV. Therefore, from the point of excitation of electrons from valency band to conduction band using a light with a long wavelength, the rutile type is more preferable than the anatase type. On the other hand, from the point of the formation of super-oxygen anion that has a strong reduction strength, the anatase type is preferable. Since the oxygen potential is positioned at 3.13 eV, the climbing up of the electrons from the bottom of the conduction band to the oxygen potential requires external energy and tends not to happen spontaneously. However, the titanium dioxide of the invention has oxidation vacancy states between the valency and conduction bands (The oxygen vacancy states in anatase type titanium dioxide were determined to be located at about 2.02-2.45 eV above the valency band). Therefore, visible light irradiation can excite electrons in the titanium dioxide of the invention from the valency band through the oxygen vacancy states to the oxygen potential, followed by forming super-oxygen ions, whatever the crystal structures are. However, rutile type titanium dioxide is preferred to anatase type titanium dioxide, because a visible light with a longer wavelength can be used in case of rutile type titanium dioxide than in case of anatase type titanium dioxide. As a result, on the titanium dioxide of the invention with anatase and/or rutile crystal structure, photocatalytic reactions such as decomposing environmental contaminants, self-cleaning surfaces of e.g. glass, lamp shades and painted car bodies and anti-fogging of surfaces can proceed at a high efficiency with visible light such as natural sunlight and fluorescence light.

The above-mentioned titanium dioxide of the invention can be preferably prepared by the following methods using Ti^{3+} ions as a precursor of the titanium dioxide.

(1) Neutralization step

Ti^{+3} solution such as TiCl_3 in hydrochloric acid solution and $\text{Ti}_2(\text{SO}_4)_3$ in sulfuric acid solution is neutralized by using a neutralization agent such as ammonia gas, NH_4OH , NaOH or KOH at 0-100°C and pH in the range of 2-10 in inert or reducing conditions in order to form titanium (III) hydroxide ($\text{Ti}(\text{OH})_3$). At a temperature higher than 100°C, it is difficult to control the formation of the nuclei of titanium hydroxide and the crystal size of the titanium dioxide of the invention. At a pH value higher than 7, the final product contains rutile type titanium dioxide, and on the other hand, at pH lower than 7, the product mainly comprises anatase type titanium dioxide. In case of neutralizing in oxidizing conditions, Ti^{+3} ions are partially oxidized into Ti^{+4} . As a result, the extent of oxygen vacancy in the titanium dioxide should be lower than that in titanium dioxide prepared in inert or reducing

conditions. Consequently, the titanium dioxide does not show a high activity with visible light. Inert conditions can also be prepared by expelling dissolved oxygen from the solution by using inert gas bubbling, and reducing conditions can be achieved by adding a reducing agent which has a higher reducing potential than $\text{Ti}^{+3} \rightarrow \text{Ti}^{+4} + \text{e}^-$ such as e.g. H_2SO_3 , formic acid, citric acid or similar.

(2) Ageing step

In the ageing step, amorphous $\text{Ti}(\text{OH})_3$ is crystallized into Ti_2O_3 and/or titanium dioxide with anatase and/or rutile type crystal structures and the supposed oxygen vacancy, depending on the ageing conditions. Ti_2O_3 does not have a good photocatalytic activity, so in the ageing step amorphous $\text{Ti}(\text{OH})_3$ must be turned into titanium dioxide with anatase and/or rutile crystal structures. By ageing at 50-150°C at a pressure ranging from atmospheric pressure to 100 bar at most, preferably 50 bar at most, for 0.1-10 hours in the same inert and/or reducing conditions as the conditions in the neutralization step, followed by washing to remove salts and drying in air or vacuum at 0-100°C, titanium dioxide with anatase and/or rutile crystal structures can be prepared with gradually forming TiO_2 crystals with oxygen vacancies. In case of neutralization at a pH value above 7, titanium dioxide with anatase and rutile crystal structures is formed in the ageing, while at a pH lower than 7 titanium dioxide with only anatase structure is prepared. In order to get a crystal size less than 10 nm, the ageing must be done at a temperature lower than 100°C. At temperatures higher than 100°C, the crystals grow too rapidly to control the crystal size and at lower than 50°C they grow too slowly to make the production practical. By ageing at high temperatures and high pressures, duration of ageing can be shortened. As a result, the preparation of the titanium dioxide of the invention can be carried out as a continuous operation, instead of a batchwise operation, resulting in improvement of cost performance. Drying should be done in air at atmospheric pressure and temperature below 50 °C or in vacuum at a temperature below 100 °C, in order to prevent destruction of oxygen vacancies. Furthermore, it is preferable that the titanium dioxide prepared by the above method is further treated at 150-500 °C in inert conditions in order to adjust the crystallinity and disperse the oxygen vacancies in the titanium dioxide.

The titanium dioxide prepared according to the invention can be used in various kinds of photocatalytic processes, e.g. for decomposing environmental contaminants, oxidizing NO into NO_2 , followed by eliminating NO_x in atmospheres, sterilizing interior walls of living rooms, self-cleaning surfaces of glass, lamp shades and painted car bodies and anti-fogging. Depending on the

process, the photocatalyst can be in many different forms. In case of decomposing environmental contaminants, a honeycomb shaped photocatalyst is normally used and the catalyst is prepared by applying a slurry composed of the titanium dioxide of the invention and inorganic/organic binders such as silica sol on a honeycomb shaped substrate. A thin film-photocatalyst is provided for sterilizing interior walls of a living space, self-cleaning surfaces of glass, lamp shades and painted car bodies and for anti-fogging, by application of a coating comprising the titanium dioxide of the invention and organo-silicon polymers as a binder.

The invention is now illustrated in greater detail with reference to examples; however, it should be understood that the invention is not deemed to be limited thereto. All the parts, percentages, and ratios are by weight unless otherwise indicated.

(1) Preparation of nanocrystalline titanium dioxide

Example 1

In 30 ml of ion-exchanged water at 25°C with nitrogen bubbling, 115 g of titanium (III) sulphate solution ($\text{Ti}_2(\text{SO}_4)_3$: 5 wt% as Ti) was dissolved. Ammonia water (NH_4OH : 2.5 wt% as NH_3) was added at the flow rate of 7.5 ml/min with stirring and nitrogen-bubbling in 30 minutes to the aqueous solution of the titanium sulphate, in order to make the pH value of the solution to be 2.0 and to form titanium hydroxide ($\text{Ti}(\text{OH})_3$). After the addition, the slurry was aged at 90°C for 4.5 hours with nitrogen-bubbling, thereby providing titanium dioxide with anatase crystal structure. The titanium dioxide thus obtained was collected by filtration and thoroughly washed with ion-exchanged water, and dried in vacuum at 25°C, thereby providing titanium oxide powder. The powder had a B.E.T. surface area of 290 m^2/g and an anatase type crystal size of 9 nm determined by line broadening of XRD peak.

Example 2

In 30 ml of ion-exchanged water at 25°C with nitrogen bubbling, 115 g of titanium (III) sulphate solution ($\text{Ti}_2(\text{SO}_4)_3$: 5 wt% as Ti) was dissolved. Ammonia water (NH_4OH : 2.5 wt% as NH_3) was added at a flow rate of 7.5 ml/min with stirring and nitrogen-bubbling in 30 minutes to the aqueous solution of the titanium sulphate, in order to make the pH value of the solution to be 7.0 and to form titanium hydroxide ($\text{Ti}(\text{OH})_3$). After the addition, the slurry was aged at 90°C for 6 hours with nitrogen-bubbling, thereby providing titanium oxide with anatase and rutile crystal structures. The titanium dioxide thus obtained was collected by filtration and

thoroughly washed with ion-exchanged water, and dried in vacuum at 25°C, thereby providing titanium dioxide powder. The powder had a B.E.T. surface area of 305 m²/g and an anatase/rutile type crystal size of 9 nm determined by line broadening of XRD peak.

5 Example 3

In 30 ml of ion-exchanged water at 25°C with nitrogen bubbling, 150 g of titanium (III) sulphate solution (Ti₂(SO₄)₃: 5 wt% as Ti) was dissolved. Ammonia water (NH₄OH: 2.5 wt% as NH₃) was added at a flow rate of 7.5 ml/min with stirring and nitrogen-bubbling in 30 minutes to the aqueous solution of the titanium sulphate, in order to make the pH value of the solution to be 5.0 and to form titanium hydroxide (Ti(OH)₃). After the addition, the slurry was aged at 70°C for one hour with nitrogen-bubbling, thereby providing titanium dioxide with anatase and rutile crystal structures. The titanium dioxide thus obtained was collected by filtration and thoroughly washed with ion-exchanged water, and dried in vacuum at 25°C, thereby providing titanium dioxide powder. The powder was then calcined at 200°C in inert atmosphere for 15 hours to grow the crystals of the titanium dioxide. The powder had a B.E.T. surface area of 301 m²/g and the crystallinity was amorphous.

Example 4

By use of the same procedure as in Example 2, titanium dioxide powder was prepared. The powder was then calcined at 350°C in inert atmosphere for 15 hours to grow the titanium oxide crystals, instead of calcination at 200°C as in Example 2. The powder had a B.E.T. surface area of 242 m²/g and a crystal (rutile type) size of 5 nm determined by line broadening of XRD peak.

Example 5

In 30 ml of ion-exchanged water at 25°C with nitrogen bubbling, 150 g of titanium (III) sulphate solution (Ti₂(SO₄)₃: 5 wt% as Ti) was dissolved. Ammonia water (NH₄OH: 2.5 wt% as NH₃) was added at a flow rate of 7.5 ml/min with stirring and nitrogen-bubbling in 30 minutes to the aqueous solution of the titanium sulphate, in order to make the pH value of the solution to be 5.0 and to form titanium hydroxide (Ti(OH)₃). After the addition, the slurry was aged at 70°C for six hours with nitrogen-bubbling, thereby providing titanium dioxide with anatase and rutile crystal structures. The titanium dioxide thus obtained was collected by filtration and thoroughly washed with ion-exchanged water, and dried in vacuum at 25°C, thereby

providing titanium dioxide powder. The powder had a B.E.T. surface area of 301 m²/g and a crystal size of 4 nm determined by line broadening of XRD peak.

Example 6

5 By use of the same procedure as in Example 5, titanium dioxide powder was provided. The powder was then calcined at 200°C in inert atmosphere for 15 hours to grow the rutile type crystals of titanium dioxide. The powder had a B.E.T. surface area of 272 m²/g and a crystal size of 6 nm determined by line broadening of XRD peak.

Example 7

10 By the use of the same procedure as in Example 5, titanium oxide powder was provided. The powder was then calcined at 350°C in inert atmosphere for 15 hours to grow the rutile type crystals of titanium dioxide. The powder had a B.E.T. surface area of 218 m²/g and a crystal size of 7 nm determined by line broadening of XRD peak.

15 Example 8

By use of the same procedure as in Example 5, titanium oxide powder was provided. The powder was then calcined at 400°C in inert atmosphere for 15 hours to grow the rutile type crystals of titanium dioxide. The powder had a B.E.T. surface area of 154 m²/g and a crystal size of 10 nm determined by line broadening
20 of XRD peak.

Example 9

By use of the same procedure as in Example 5, titanium dioxide powder was prepared. The powder was then calcined at 500°C in inert atmosphere for 15 hours to grow the rutile type crystals of titanium dioxide. The powder had a B.E.T.
25 surface area of 111 m²/g and a crystal size of 14 nm determined by line broadening of XRD peak.

Example 10

In 30 ml of ion-exchanged water at 25°C with nitrogen bubbling, 152 g of titanium
30 (III) sulphate solution (Ti₂(SO₄)₃: 5 wt% as Ti) was dissolved. Ammonia water (NH₄OH: 2.5 wt% as NH₃) was added at a flow rate of 7.5 ml/min with stirring and nitrogen-bubbling in 30 minutes to the aqueous solution of the titanium sulphate, in

order to make the pH value of the solution to be 5.0 and to form titanium hydroxide ($\text{Ti}(\text{OH})_3$). After the addition, the slurry was aged at 95°C for two hours with nitrogen-bubbling, thereby providing titanium dioxide with anatase crystal structure. The titanium dioxide thus obtained was collected by filtration and
5 thoroughly washed with ion-exchanged water, and dried in vacuum at 25°C, thereby providing titanium dioxide powder with antase type crystal structure. The powder was then calcined at 200°C in inert atmosphere for 15 hours to grow the anatase type crystals of titanium dioxide. The powder had a B.E.T. surface area of 240 m²/g and a crystal size of 13 nm determined by line broadening of XRD peak.

10 Example 11

By use of the same procedure as in Example 10, titanium dioxide powder was prepared with antase type crystal structure. The powder was then calcined at 350°C in inert atmosphere for 15 hours to grow the anatase type crystals of titanium dioxide. The powder had a B.E.T. surface area of 190 m²/g and a crystal size of
15 15 nm determined by line broadening of XRD peak.

Example 12 (comparative)

By use of the same procedure as in Example 10, titanium dioxide powder was prepared with antase type crystal structure. The powder was then calcined at 350°C in 10% NH_3 atmosphere for 15 hours to grow and reduce the anatase type crystals
20 of titanium dioxide. The powder had a B.E.T. surface area of 145 m²/g and a crystal size of 19 nm determined by line broadening of XRD peak.

Example 13 (comparative)

An anatase type titanium dioxide powder (ST-01 available from Ishihara Sangyo) had a B.E.T. surface area of 236 m²/g and a crystal size of 12 nm determined by line
25 broadening of XRD peak.

(2) Photocatalytic activity test

The flow reactor consisted of a stainless steal vessel (500 cm³) equipped with a MSF-44A monochromatic light source using a 150 W xenon lamp (wave length: 180-850 nm) and a GG-455 light filter (50% of the light shorter than 455 nm is cut;
30 available from SCHOTT) was used to evaluate the photocatalytic activity in connection with oxidation of acetaldehyde. 0.3 g of powdery titanium dioxide and two drops of silica sol (Nissan Chemical: Snow tex-N) were mixed and milled by

hand with an agate mortar to prepare a slurry for coating. A sheet of glass fiber tissue with 40 mm of diameter was coated with the slurry at a coating weight of 0,1g. The sheet was placed in the vessel and 200 ppm of acetaldehyde, which was balanced with the gas mixture of 21% of oxygen and 79% of nitrogen, was prepared by injection of 25 wt% acetaldehyde water solution. First, without light source, the concentration of acetaldehyde in the vessel was monitored with time. With time, the concentration normally decreased, then the acetaldehyde water solution was additionally injected and when the 200 ppm of the concentration was stabilized, the source was turned on, the concentration was monitored using a gas chromatography with an FID detector (Hewlett Packard 5890), and acetaldehyde decomposition rate in two hours was calculated by use of the following equation.

The decomposition rate = decrease of peak area/120 minutes: the line slope determined by a linear regression method.

The results are shown in Table 1.

Table 1

Catalyst	Decomposition rate
Example 1	22
Example 2	30
Example 3	43
Example 4	70
Example 5	45
Example 6	89
Example 7	141
Example 8	186
Example 9	149
Example 10	116
Example 11	132
Example 12	15
Example 13	3

Claims

1. A method for the preparation of a titanium dioxide photocatalyst, **characterized** in that the method comprises producing a titanium (III) containing solid precipitate from a solution containing titanium (III) ions in inert or
5 substantially non-oxidizing conditions, separating precipitated solids from the liquid phase, and calcinating the separated solids at an elevated temperature so as to obtain a photocatalyst product having a crystal size in the range of 5 – 50 nm.
2. A method according to claim 1, **characterized** in that precipitation takes place at a temperature of 0 – 115°C, preferably 50 – 100°C.
- 10 3. A method according to claim 1 or 2, **characterized** in that precipitation is achieved by addition of a base to the titanium (III) ion solution.
4. A method according to claim 3, **characterized** in that the base is ammonia gas, ammonium hydroxide, an alkali or earth alkali metal hydroxide or a mixture thereof.
- 15 5. A method according to claim 3 or 4, **characterized** in that addition of the base raises the pH of the solution to the range of 2 – 10.
6. A method according to any one of the preceding claims, **characterized** in that the titanium (III) containing precipitate is aged in liquid medium in inert or non-oxidizing conditions for 0.1 – 10 hours before it is subjected to calcination.
- 20 7. A method according to claim 6, **characterized** in that ageing takes place at a temperature of 50 – 150°C under a pressure, which is at most 100 bar.
8. A method according to claim 6 or 7, **characterized** in that precipitation is followed by ageing of the solid precipitate in the same liquid phase.
9. A method according to any one of the preceding claims, **characterized** in that
25 at the precipitation and/or ageing steps inert or non-oxidizing conditions are maintained by bubbling inert gas through the solution.
10. A method according to any one of claims 1 – 8, **characterized** in that at the precipitation and/or ageing steps reducing conditions are produced by addition of a reducing agent.

11. A method according to any one of the preceding claims, **characterized** in that calcination is carried out at a temperature of 100 – 500°C.
12. A method according to claim 11, **characterized** in that calcination takes place in an inert atmosphere.
- 5 13. A titanium dioxide photocatalyst, **characterized** in that it comprises particles having the crystal structure of rutile and/or anatase and a crystal size in the range of 5 – 50 nm.
14. A photocatalyst according to claim 13, **characterized** in that the crystal size is in the range of 5 – 20 nm.
- 10 15. Use of a photocatalyst according to claim 13 or 14 to catalyse decomposition of organic compounds or microorganisms.
16. Use of a photocatalyst according to claim 13 or 14, in a mixture with a binder as a coating applicable onto a substrate.
- 15 17. Use according to claim 16, **characterized** in that the substrate is a honeycomb catalysator structure.
18. Use according to claim 16 as a component of a paint for car bodies.
19. Use according to claim 16 as a component of a self-cleaning surface coating.
20. Use according to claim 16 in a coating for glass, lamps or shades.
21. Use according to claim 16 for anti-fogging.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 02/00985

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01G 23/047, B01J 21/06, B01J 37/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C01G, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL, PAJ, COMPDX, KA.ABS.DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1254863 A1 (ECODEVICE LABORATORY CO., LTD), 6 November 2002 (06.11.02), see paragraph 0003, 0004, 0026, 0027, 0030; embodiment 1,4,6 --	1-21
X	EP 1095908 A1 (SUMITOMO CHEMICAL COMPANY, LIMITED), 2 May 2001 (02.05.01), see section 0031, 0041 --	1-21
X	EP 1065169 A1 (SUMITOMO CHEMICAL COMPANY, LIMITED), 3 January 2001 (03.01.01), see section 0001, 0031, 0033, 0047 --	1-21

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

20 February 2003

Date of mailing of the international search report

21 -02- 2003

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Lars Wallentin/MP

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP 02/00985

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 1178011 A1 (SUMITOMO CHEMICAL COMPANY, LIMITED), 6 February 2002 (06.02.02), claims 1-5, see section, 0004, 0008, 0011, 0012, 0014-0021 --	1-21
A	EP 0675086 A2 (ISHIHARA SANGYO KAISHA, LTD.), 4 October 1995 (04.10.95), page 2, line 40 - line 51; page 3, line 36 - line 55; page 4, line 29 - line 32, see example 1 --	1-21
A	CA 2342523 A1 (SUMITOMO CHEMICAL COMPANY, LIMITED, JP), 24 November 2001 (24.11.01), example 1 --	1-21
A	EP 1138634 A1 (SUMITOMO CHEMICAL COMPANY, LIMITED), 4 October 2001 (04.10.01), paragraph (0004), example 1 --	1-21
A	US 5011674 A (MASAFUMI YOSHIMOTO ET AL), 30 April 1991 (30.04.91), see example 1 --	1-21
A	Journal of Photochemistry and Photobiology A:, Volume 144, 2001, A.V. Vorontsov et al, "CORRELATION OF TiO2 PHOTOCATALYTIC ACTIVITY AND DIFFUSE REFLECTANCE SPECTRA", page 193 - page 196, see abstract experimental -- -----	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

30/12/02

International application No.

PCT/FI 02/00985

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1254863 A1	06/11/02	AU 2884901 A JP 3215698 B JP 2002255554 A JP 2002255555 A JP 2002331225 A WO 0156928 A	14/08/01 09/10/01 11/09/02 11/09/02 19/11/02 09/08/01
EP 1095908 A1	02/05/01	AU 6669700 A CN 1294157 A JP 2001190953 A JP 2002166179 A JP 2001316116 A	03/05/01 09/05/01 17/07/01 11/06/02 13/11/01
EP 1065169 A1	03/01/01	AU 3939100 A CA 2311980 A CN 1280034 A JP 2001072419 A	04/01/01 30/12/00 17/01/01 21/03/01
EP 1178011 A1	06/02/02	AU 3140401 A CN 1336326 A JP 2002047012 A JP 2002249319 A	07/02/02 20/02/02 12/02/02 06/09/02
EP 0675086 A2	04/10/95	AT 147366 T AU 659013 B AU 4216893 A CA 2101360 A CN 1036845 B CN 1093060 A CN 1159466 A DE 69307208 D,T DK 581216 T EP 0581216 A,B SE 0581216 T3 ES 2096152 T JP 6293519 A JP 7000819 A JP 7012539 U SG 42893 A JP 7002522 A	15/01/97 04/05/95 03/02/94 29/01/94 31/12/97 05/10/94 17/09/97 05/06/97 30/06/97 02/02/94 01/03/97 21/10/94 06/01/95 03/03/95 17/10/97 06/01/95
CA 2342523 A1	24/11/01	AU 3140501 A CN 1324766 A EP 1160202 A JP 2001335321 A US 2001056037 A	29/11/01 05/12/01 05/12/01 04/12/01 27/12/01
EP 1138634 A1	04/10/01	AU 3140601 A CA 2342566 A CN 1319562 A JP 2001278625 A US 2002012628 A JP 2001278626 A JP 2001302241 A JP 2001354422 A	04/10/01 30/09/01 31/10/01 10/10/01 31/01/02 10/10/01 31/10/01 25/12/01

Information to patient family members

30/12/02

International application No.

PCT/FI 02/00985

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5011674 A	30/04/91	JP 1301518 A	05/12/89
		JP 1814428 C	18/01/94
		JP 5024866 B	09/04/93
		US 5169619 A	08/12/92
